

Chapter 14: Chemical Kinetics

Kahoot!

1. The rate of a reaction can be increased by: increasing reactant concentrations, increasing temperature, adding a suitable catalyst, **all of the above**
2. Over time, the rate of most chemical reactions tends to _____. Increase, **decrease**, remain constant, oscillate
3. Consider the reaction $A_3 + 3B_2 \rightarrow 3AB_2$. If A_3 consumption is -0.750 M/min , then B_2 consumption is: -0.750 M/min , -0.225 M/min , -0.250 M/min , **-2.25 M/min**
4. If tripling the concentration of reactant A multiplies the rate by a factor of 9, the reaction is ____ order in A. 0, 1, **2**, 3
5. What are the correct units for k of a 5th order reaction? $\text{M}^{-2} \text{s}^{-1}$, $\text{M}^{-3} \text{s}^{-1}$, **$\text{M}^{-4} \text{s}^{-1}$** , $\text{M}^{-5} \text{s}^{-1}$
6. If $\text{Rate} = k[A][B]$, what is the overall order of this reaction? 1, **2**, 3, 4
7. If $W + X \rightarrow Y + Z$, $\text{Rate} = k[W]$, what is the reaction order for X? **0**, 1, 2, 3
8. Select the incorrect statement:
 - the orders are not taken from the coefficients in the balanced eqn
 - for a 1st-order reaction, a plot of $\ln[A]$ versus t is linear
 - **for a 0th-order reaction, a plot of [A] versus t is parabolic**
 - the overall order of a 0th order reaction is 0
9. The time required for the concentration of a reactant to be reduced by half is _____. Midpoint of the reaction, equivalence point of the reaction, half-rate of the reaction, **half-life of the reaction**
10. If a reaction is 1st order in [A], which of the following will yield a linear plot? [A] vs time, $1/[A]$ vs time, **$\ln[A]$ vs time**, $[A]^2$ vs time
11. If a reaction is 2nd order in [A] which of the following will yield a linear plot? [A] vs time, **$1/[A]$ vs time**, $\ln[A]$ vs time, $[A]^2$ vs time
12. If a reaction is 0th order in [A] which of the following will yield a linear plot? **[A] vs time**, $1/[A]$ vs time, $\ln[A]$ vs time, $[A]^2$ vs time
13. ____ is the minimum energy required for a collision between molecules to generate product. Initial energy, internal energy, external energy, **energy of activation**
14. The rate-determining step is the ____ step in a reaction mechanism. First, last, fastest, **slowest**
15. In a reaction mechanism, a species that is produced then consumed is _____. A byproduct, a catalyst, **an intermediate**, a reactant
16. What is the molecularity of $H_2 + NO \rightarrow N + H_2O$? unimolecular, **bimolecular**, trimolecular, termolecular
17. What is the rate law for elementary step $H_2 + NO \rightarrow N + H_2O$? $\text{rate} = k[H]^2[NO]$, **$\text{rate} = k[H_2][NO]$** , $\text{rate} = k[H_2][N][O]$, $\text{rate} = k[H]^2[NO] - [N][H_2O]$
18. In a reaction mechanism, a species that is consumed then produced is _____. A byproduct, a **catalyst**, an intermediate, a reactant
19. Adding a catalyst increases the rate of a reaction by: increasing molecular velocities, increasing molecular collisions, decreasing the energy of activation, **all of the above**

Whiteboard Examples

Experimental Determination Example: Determine the rate law, the rate constant and the reaction orders for each reactant and the overall reaction order using the data given below.

Experiment	[A] ₀	[B] ₀	Initial Rate M/s
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}

3	0.200	0.100	16.0×10^{-5}
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In other words we want to find, m, n, and k for rate = $k[A]^m[B]^n$

Comparison of 1 & 2 indicates that changes in [B] has no impact – let's prove it

$$\frac{rate_1}{rate_2} = \frac{k[A]_1^m [B]_1^n}{k[A]_2^m [B]_2^n}$$

$$\frac{4.0 \times 10^{-5} \frac{M}{s}}{4.0 \times 10^{-5} \frac{M}{s}} = \frac{k(0.100M)^m (0.100M)^n}{k(0.100M)^m (0.200M)^n}$$

$$1 = \left(\frac{1}{2}\right)^n \rightarrow n = 0 \text{ which means } rate = k[A]^m [B]^0 = rate = k[A]^m$$

Now we need to find m by picking two experiments in which [A] changes let's use 2 & 3

$$\frac{rate_2}{rate_3} = \frac{k[A]_2^m}{k[A]_3^m}$$

$$\frac{4.0 \times 10^{-5} \frac{M}{s}}{16.0 \times 10^{-5} \frac{M}{s}} = \frac{k(0.100M)^m}{k(0.200M)^m}$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^m \rightarrow m = 2 \text{ which means } rate = k[A]^2$$

Finally we can use any of the three trials to find our constant k and plug them into the rate law.

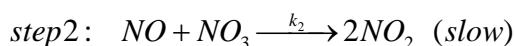
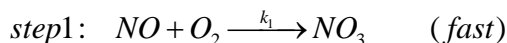
$$rate = k[A]^2$$

$$4.0 \times 10^{-5} \frac{M}{s} = k(0.100M)^2 \rightarrow k = \frac{4.0 \times 10^{-5} \frac{M}{s}}{0.0100M^2} = 4.0 \times 10^{-3} M^{-1} s^{-1}$$

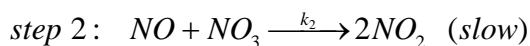
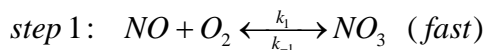
Putting it all together we get a rate law of:

$$rate = 4.0 \times 10^{-3} M^{-1} s^{-1} [A]^2$$

Example for Fast Equilibrium Approximation: What is the rate law for the mechanism below?



-- when a fast step precedes the slow step we assume the fast step is in eq or reversible



-- we can then write the rate of step1 as rate = $k_1[NO][O_2] = k_{-1}[NO_3]$
solving for $[NO_3]$,

$$[NO_3] = \frac{k_1}{k_{-1}}[NO][O_2]$$

-- the rate for step2: rate = $k_2[NO][NO_3]$

we can plug in the relationship from step1 into this equation,

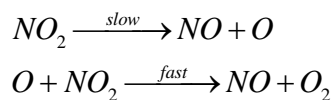
$$rate = k_2[NO] \frac{k_1}{k_{-1}}[NO][O_2] = k_2 \frac{k_1}{k_{-1}}[NO]^2[O_2]$$

Applied Fast Equilibrium Example: The rate laws for the thermal and photochemical decomposition of NO_2 are different. Which of the following mechanisms are possible for thermal and photochemical rates given the information below?

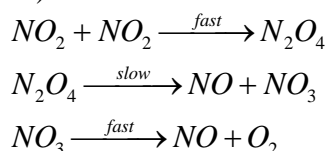
Thermal rate = $k[NO_2]^2$

Photochemical rate = $k[NO_2]$

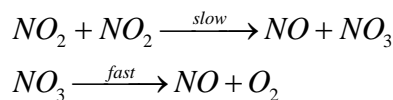
a.)



b.)



c.)



a.) rate = $k[NO_2]$ which is consistent with the photochemical rate

b.) fast step before slow so we assume eq:

$$NO_2 + NO_2 \xrightleftharpoons[k_{-1}]{k_1} N_2O_4 \quad k_1[NO_2]^2 = k_{-1}[N_2O_4] \rightarrow [N_2O_4] = \frac{k_1}{k_{-1}}[NO_2]^2$$

$$N_2O_4 \xrightarrow{k_2} NO + NO_3 \quad rate = k_2[N_2O_4] = k_2 \frac{k_1}{k_{-1}}[NO_2]^2$$

therefore this mechanism is consistent with the thermal rate

c.) rate = $k[NO_2]^2$ which is also consistent with the thermal rate